

539, 218

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number
WO 2004/060952 A1

- (51) International Patent Classification⁷: C08G 18/12, 18/28, 18/48, C09D 175/04, C09J 175/04
- (21) International Application Number: PCT/US2003/038510
- (22) International Filing Date: 5 December 2003 (05.12.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10/325,007 20 December 2002 (20.12.2002) US
- (71) Applicant (for all designated States except US): **BAYER POLYMERS LLC** [US/US]; 100 Bayer Road, Pittsburgh, PA 15205-9741 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **ROESLER, Richard, R.** [US/US]; 863 Hillcrest Circle, Wexford, PA 15090 (US). **CRAWFORD, Derek, L.** [US/US]; 678 Gamble Road, Oakdale, PA 15071 (US).
- (74) Agents: **MATZ, Gary, F.** et al.; 100 Bayer Road, Pittsburgh, PA 15052 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A PROCESS FOR THE PREPARATION OF MOISTURE-CURABLE, POLYETHER URETHANES WITH TERMINAL CYCLIC UREA/REACTIVE SILANE GROUPS

(57) Abstract: A process for preparing a moisture-curable, polyether urethane containing terminal cyclic urea/reactive silane groups by reacting at an NCO:OH equivalent ratio of 1.5:1 to 2.5:1 a) a hydroxyl component containing i) a polyether containing two hydroxyl groups and one or more polyether segments, wherein the polyether segments have a number average molecular weight of at least 3000 and a degree of unsaturation of less than 0.04 milliequivalents/g, and ii) a polyether containing one hydroxyl group and one or more polyether segments having a number average molecular weight of 1000 to 15,000, with b) an isocyanate component containing i) a compound containing two isocyanate groups, and ii) a compound containing one isocyanate group, and subsequently reacting this reaction product at an equivalent ratio of isocyanate groups to isocyanate-reactive groups of 0.8:1 to 1.1:1 with c) a compound containing an aspartate group and a reactive silane group to form an intermediate polyether urethane containing terminal non-cyclic urea/reactive silane groups and converting the non-cyclic urea groups to cyclic urea groups by reacting the intermediate polyether urethane.

WO 2004/060952 A1

A PROCESS FOR THE PREPARATION OF
MOISTURE-CURABLE, POLYETHER URETHANES WITH
TERMINAL CYCLIC UREA/REACTIVE SILANE GROUPS

FIELD OF THE INVENTION

The present invention relates to a process for preparing moisture-curable polyether urethanes containing terminal cyclic urea/reactive silane groups from polyether polyols having a low degree of unsaturation and to the use of these polyether urethanes as sealants, adhesives and coatings.

BACKGROUND OF THE INVENTION

Polyether urethanes containing reactive silane groups, also referred to as silane-terminated polyurethanes (STPs), and their use as sealants and adhesives are known and described, e.g., in U.S. Patents 5,554,709; 4,857,623; 5,227,434 and 6,197,912; and WO 02/06367. The silane-terminated polyurethanes may be prepared by various methods. In one method the silane-terminated polyurethanes are prepared by reacting diisocyanates with polyether polyols to form isocyanate-terminated prepolymers, which are then reacted with aminosilanes to form the silane-terminated polyurethanes. The sealants may also be prepared by reacting unsaturated monools with diisocyanates to form intermediates containing unsaturated end groups and then converting these unsaturated groups to alkoxy silane groups by hydrosilylation. In another method the sealants are prepared in one step by the reaction of polyether diols with isocyanatosilanes

To be useful as sealants the silane-terminated polyurethanes should have a number average molecular weight of 6000 to 20,000. One method of obtaining this molecular weight is to use polyether diols prepared by the KOH process and having a molecular weight of 2000 to prepare the isocyanate-terminated prepolymers. The presence of urethane groups causes the products to have a high viscosity. To achieve suitable

application viscosities, the high viscosity is reduced by the addition of higher amounts of plasticizer and lesser amounts of fillers, resulting in more expensive sealant products.

Another method of obtaining high molecular weight sealants is by using high molecular weight polyether diols having a low degree of unsaturation and prepared using special catalysts as described in EP-A 0,546,310, EP-A 0,372,561 and DE-A 19,908,562. When these polyether diols are used, the resulting sealants have excellent tensile strength, but the sealants are too brittle for many applications because the elongation is too low and the 100% modulus is too high.

The preparation of sealants from mixtures of polyfunctional and monofunctional silane-terminated polyurethanes is known and disclosed in U.S. Patents 5,554,709 and 4,857,623 and WO 02/06367. However, these references do not disclose the use of polyether polyols having a low degree of unsaturation and aspartate-functional silanes to prepare the sealants.

The preparation of silane-terminated polyether urethanes from aspartate-functional silanes is disclosed in U.S. Patent 5,364,955 and WO 98/18843. In both of these references the polyethers used to prepare polyether urethanes do not have a low degree of unsaturation. In addition, mixtures of polyfunctional and monofunctional silane-terminated polyurethanes are not disclosed. Finally, in the latter reference the polyethers must contain 15 to 40% by weight of ethylene oxide units.

WO 00/26271 discloses the preparation of silane-terminated polyether urethanes from polyether polyols having a low degree of unsaturation and aspartate-functional silanes. The products are prepared by reacting diisocyanates with high molecular weight polyether diols to form NCO prepolymers, which are then capped with aspartate-functional silanes to form silane-terminated polyether urethanes. This application does not disclose mixtures of disilane-terminated polyether urethanes with polyether urethanes containing one reactive silane group.

U.S. Patent 6,265,517 describes a similar process for preparing silane-terminated polyether urethanes from polyether polyols having a low degree of unsaturation and aspartate-functional silanes. The patent requires the starting polyol to have a monool content of less than

5 31 mole%, and teaches that a relatively high monool content is highly undesirable because monools react with isocyanates thereby reducing crosslinking and curing of the prepolymer. The patent also requires the aspartate silanes to be prepared from dialkyl maleates in which the alkyl groups each contain more than four carbon atoms.

10 EP 0,372,561 discloses polyether urethanes containing reactive silane groups and prepared from polyether polyols having a low degree of unsaturation. In addition, polyether urethanes containing one reactive silane group are disclosed. This application fails to disclose the use of aspartate-functional silanes to incorporate the reactive silane groups.

15 The deficiencies of the preceding sealants were overcome in copending applications, U.S. Serial Nos. 10/690,751, 10/690,955, 10/690,956, 10/690,954 and 10/690,931, which describe moisture-curable, alkoxy silane-functional polyether urethanes containing both polyether urethanes having two or more reactive silane groups and polyether
20 urethanes having one reactive silane group. The moisture-curable polyether urethanes are suitable for use as sealants, adhesives and coatings which possess high tensile strengths and elongations and have a reduced 100% modulus when compared with existing products.

25 In the copending applications the polyether urethane component containing two or more reactive silane groups is prepared from high molecular weight polyether polyols having a low degree of unsaturation. In addition, at least a portion of the reactive silane groups present in at least one of the two components are incorporated by the use of silanes containing secondary amino groups. Finally, the polyether urethane

components described in the copending applications are prepared separately and subsequently blended to form the moisture-curable polyether urethanes according to the invention.

Copending application, U.S. Serial No. 10/690,953 describes a
5 process for simultaneously preparing moisture-curable polyether urethanes containing a mixture of polyether urethane component having two or more reactive silane groups and a polyether urethane component having one reactive silane group instead of being prepared separately and mixed. The mixture of polyether urethanes retains all of the valuable
10 properties of the polyether urethanes disclosed in the previously described copending applications.

A disadvantage of the moisture-curable polyether urethanes described in the preceding copending applications is that they are not storage stable at moderately elevated temperatures of 50 to 90°C, which
15 may be present in a drum stored in a hot climate.

Accordingly, it is an object of the present invention to provide a process for preparing moisture-curable polyether urethanes at lower production viscosities, in which the resulting products are storage stable at elevated temperatures and also retain all of the valuable properties of the
20 polyether urethanes disclosed in the preceding copending applications, i.e., the products are suitable for use as sealants, adhesives and coatings which possess high tensile strengths and elongations and have a reduced 100% modulus.

This object may be achieved with the process of the present
25 invention in which the moisture-curable polyether urethanes containing a mixture of polyether urethane component having two or more reactive silane groups and a polyether urethane component having one reactive silane group are prepared simultaneously and in which the polyether urethanes contain terminal cyclic urea/reactive silane groups.

The present invention is based on the surprising discovery that the non-cyclic urea groups formed by the reaction of isocyanate groups and aspartate silane groups decompose back into the starting components when stored at moderately elevated temperatures. In accordance with the present invention this decomposition is prevented by converting the non-cyclic urea groups into cyclic urea groups, which are thermally stable.

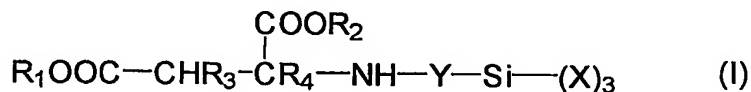
It is surprising that the polyether urethanes obtained according to the process of present invention can be used to prepare cured resins that possess the same properties as those obtained in accordance with the copending applications because the presence of cyclic urea groups would be expected to result in less flexible cured resins that would not have the same elongation and 100% modulus as cured resins prepared from polyether urethanes containing non-cyclic urea groups.

SUMMARY OF THE INVENTION

The present invention relates to a process for preparing a moisture-curable, polyether urethane containing terminal cyclic urea/reactive silane groups by reacting at an NCO:OH equivalent ratio of 1.5:1 to 2.5:1

- a) a hydroxyl component containing
 - i) 20 to 100% by weight, based on the weight of component a), of a polyether containing two hydroxyl groups and one or more polyether segments, wherein the polyether segments have a number average molecular weight of at least 3000 and a degree of unsaturation of less than 0.04 milliequivalents/g, provided that the sum of the number average molecular weights of all of the polyether segments per molecule averages 6000 to 20,000, and
 - ii) 0 to 80% by weight, based on the weight of component a), of a polyether containing one hydroxyl group and one or more polyether segments having a number average molecular weight of 1000 to 15,000, with
- b) an isocyanate component containing

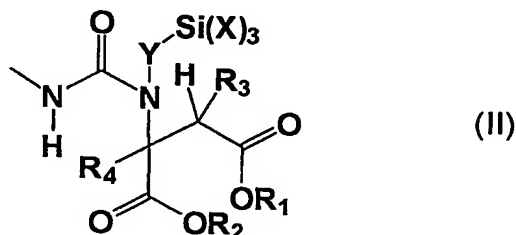
- i) 20 to 100% by weight, based on the weight of component b), of a compound containing two isocyanate groups, and
- ii) 0 to 80% by weight, based on the weight of component b), of a compound containing one isocyanate group,
- 5 provided that total percentages of a-ii) and b-ii) add up to at least 10, to form an isocyanate-containing reaction product and subsequently reacting this reaction product at an equivalent ratio of isocyanate groups to isocyanate-reactive groups of 0.8:1 to 1.1:1 with
- c) a compound containing an isocyanate-reactive group and one
- 10 reactive silane groups in which at least 10 mole % of component c) is a compound corresponding to the formula



wherein

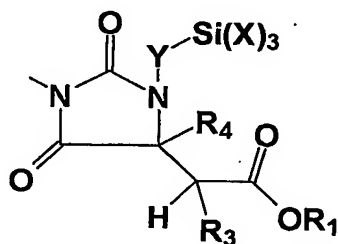
- 20 X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least two of these groups are alkoxy or acyloxy groups,
- Y represents a linear or branched alkylene group containing 1
- 25 to 8 carbon atoms,
- R₁ and R₂ are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less and
- R₃ and R₄ are identical or different and represent hydrogen or
- 30 organic groups which are inert towards isocyanate groups at a temperature of 100°C or less,

to form an intermediate polyether urethane containing at least a portion of terminal non-cyclic urea/reactive silane groups corresponding to formula II

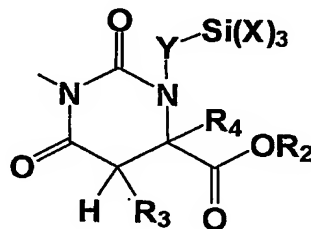


5

and converting the non-cyclic urea groups to cyclic urea groups by reacting the intermediate polyether urethane in the presence of an acid catalyst and heat to form terminal cyclic urea/reactive silane groups corresponding to formula III and/or formula IV



Formula III



Formula IV

10

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention the term "reactive silane group" means a silane group containing at least two alkoxy or acyloxy groups as defined by substituent "X". A silane group containing two or three alkoxy and/or acyloxy groups is considered to be one reactive silane group. Also, a urethane is a compound containing one or more urethane and/or urea groups. These compounds preferably contain one or more urethane groups and may optionally contain urea groups. More preferably, these compounds contain both urethane and urea groups.

15

20

The isocyanate-containing reaction products used for preparing the moisture-curable polyether urethanes may be prepared by several methods. For example, they may be prepared by reacting a mixture of polyether diol a-i) and polyether monool a-ii) with an excess of diisocyanate b-i), to form an isocyanate-containing reaction product containing NCO prepolymers and monoisocyanates formed by the reaction of one mole of a diisocyanate with one mole of a polyether monool. In this embodiment polyether monool a-ii) is present in an amount of at least 10% by weight, based on the weight of component a).

10 In another embodiment the isocyanate-containing reaction products are prepared by reacting polyether diol a-i) with an excess of diisocyanate b-i) and monoisocyanate b-ii) to form an isocyanate-containing reaction product containing NCO prepolymers and monoisocyanates formed by the reaction of one mole of a monoisocyanate and one mole of a diisocyanate with one mole of a polyether diol. In this embodiment monoisocyanate b-ii) is present in an amount of at least 10% by weight, based on the weight of component b).

20 It is also possible to use a combination of the preceding processes in which both polyether monools a-ii) and monoisocyanates b-ii) are present.

The isocyanate-containing reaction products are prepared by reacting the isocyanate component with the polyether component at an NCO:OH equivalent ratio of a 1.5:1 to 2.5:1, preferably 1.8:1 to 2.2:1 and more preferably 1.9:1 to 2.1:1 and most preferably 2:1. It is especially preferred to react one mole of the isocyanate component for each equivalent of hydroxyl groups.

25 When preparing the isocyanate-containing reaction product from diisocyanate b-i), polyether diol a-i) and polyether monool a-ii) at an NCO:OH equivalent ratio of 2:1, the reaction mixture contains the 2/1 adduct of the diisocyanate and diol; minor amounts of higher molecular weight oligomers, such as the 3/2 adduct; a monoisocyanate, which is the

1/1 adduct of the monool and diisocyanate; non-functional polymers, which are formed by the reaction of two molecules of the monool with one molecule of the diisocyanate; various products containing both diols and monools; and a minor amount of unreacted diisocyanate, which can be removed, e.g., by distillation, or which can remain in the reaction mixture.

To form the moisture-curable polyether urethanes according to the invention the isocyanate-containing reaction products are reacted with compounds c) containing reactive silane groups at equivalent ratio of isocyanate groups to isocyanate-reactive groups of 0.8:1 to 1.1:1, preferably 0.9:1 to 1.05:1 and more preferably about 1:1.

The moisture-curable polyether urethanes may also be prepared by reacting an excess of diisocyanates b) with aminosilanes c) to form a monoisocyanate and then reacting the resulting monoisocyanate with a mixture of polyethers a-i) and a-ii) to form the polyether urethanes.

The moisture-curable, polyether urethanes obtained according to the process of the present invention contain polyether urethanes A), which contain two or more, preferably two, reactive silane groups, and polyether urethanes B), which contain one reactive silane group. Also present are polymers C), which are the reaction products of unreacted isocyanates b) with aminosilanes c). Polymers C) are preferably present in an amount of less than 5% by weight.

The reaction mixture also contains non-functional polymers D), which are formed by the reaction of two molecules of the monool with one molecule of the diisocyanate, two molecules of the monoisocyanate with one molecule of the diol, or one molecule of the monool with one molecule of a monoisocyanate. Non-functional polymers D) are generally present in an amount of less than 30% by weight.

In accordance with the present invention it is also possible to adjust the NCO:OH equivalent ratio to form additional amounts of non-functional polymers D) are formed from the reactants as previously described.

These polymers remain in the reaction mixture and function as plasticizers during the subsequent use of the moisture-curable, polyether urethanes according to the invention.

Suitable polyethers for use as component a-i) include polyoxy-
5 propylene polyethers containing two hydroxyl groups and optionally up to 20% by weight, based on the weight of component a-i), of polyethers containing more than 2 hydroxyl groups. The polyethers contain one or more, preferably one, polyether segment having a number average
10 molecular weight of 3000 to 20,000, preferably 6000 to 15,000 and more preferably 8000 to 12,000. When the polyether segments have a number average molecular weight of 3000, for example, then two or more of these segments must be present so that the number average molecular weights of all of the polyether segments per molecule averages 6000 to 20,000.

Suitable polyols for preparing polymers a) are polyether polyols, in
15 some cases polyoxypropylene polyols, in many instances diols, having a number average molecular weight of 3000 to 20,000, preferably 6000 to 15,000, and more preferably 8000 to 12,000. The polyethers can have a maximum total degree of unsaturation of less than 0.04 milliequivalents/g, in some cases less than 0.02 meq/g (meq/g), in other cases less than
20 0.01 meq/g and in some situations 0.007 meq/g or less. The amount of unsaturation will vary depending on the method used to prepare the polyether as well as the molecular weight of the polyether. Such polyether diols are known and can be produced, as a non-limiting example, by the propoxylation of suitable starter molecules. As another
25 non-limiting example, minor amounts (up to 20% by weight, based on the weight of the polyol) of ethylene oxide can be used. If ethylene oxide is used, it can be used as the initiator for or to cap the polypropylene oxide groups. Non-limiting examples of suitable starter molecules include diols such as ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol,
30 1,6 hexanediol and 2-ethylhexanediol-1,3. Also suitable are polyethylene glycols and polypropylene glycols.

Suitable methods for preparing polyether polyols are known and are described, for example, in EP-A 283 148, US-A 3 278 457, US-A 3 427 256, US-A 3 829 505, US-A 4 472 560, US-A 3 278 458, US-A 3 427 334, US-A 3 941 849, US-A 4 721 818, US-A 3 278 459, 5 US-A 3 427 335 and US-A 4 355 188. They are preferably prepared using double metal cyanides as catalysts.

In addition to the polyether polyols, minor amounts (up to 20% by weight, based on the weight of the polyol) of low molecular weight dihydric and trihydric alcohols having a molecular weight 32 to 500 can also be 10 used. Suitable examples include ethylene glycol, 1,3-butandiol, 1,4-butandiol, 1,6-hexandiol, glycerine or trimethylolpropane. However, the use of low molecular weight alcohols is less preferred.

Polyethers a-i) are present in a amount of 20 to 100% by weight. When polyether monools a-ii) are used as the sole monofunctional 15 component, polyethers a-i) are present in a minimum amount of 20% by weight, preferably 30% by weight and more preferably 40% by weight, and a maximum amount of 100% by weight, preferably 90% by weight, more preferably 80% by weight and most preferably 70% by weight. The preceding percentages are based on the total weight of polyethers a).

20 Suitable polyether monools a-ii) are polyether monools having a number average molecular weight of 1000 to 15,000, preferably 3000 to 12,000 and more preferably 6000 to 12,000. The polyether monools are prepared by the alkoxylation of monofunctional starting compounds with alkylene oxides, preferably ethylene oxide, propylene oxide or butylene 25 oxide, more preferably propylene oxide. If ethylene oxide is used, it is used in an amount of up to 40% by weight, based on the weight of the polyether. The polyethers are preferably prepared either by the KOH process or by mixed metal cyanide catalysis. The latter process results in products with low a degree of unsaturation.

In many cases, the polyethers, which as a non-limiting example can be polypropylene oxide polyethers have a maximum total degree of unsaturation of less than 0.04 milliequivalents/g (meq/g) in some cases less than 0.02 meq/g, in other cases less than 0.01 meq/g and in some situations 0.007 meq/g or less. The amount of unsaturation will vary depending on the method used to prepare the polyether as well as the molecular weight of the polyether.. Such polyether monools are known and can be produced, as a non-limiting example by the methods set forth previously for preparing polyethers, a non-limiting example being the polyoxypropylene polyols by the propoxylation of suitable starter molecules. In another non-limiting example, minor amounts (up to 20% by weight, based on the weight of the polyol) of ethylene oxide can also be used. As with the polyethers a-i), if ethylene oxide is used, it can be used as the initiator for or to cap the polypropylene oxide groups.

Examples of suitable starter molecules include aliphatic, cycloaliphatic and araliphatic alcohols, phenol and substituted phenols, such as methanol, ethanol, the isomeric propanols, butanols, pentanols and hexanols, cyclohexanol and higher molecular weight compounds such as nonylphenol, 2-ethylhexanol and a mixture of C₁₂ to C₁₅, linear, primary alcohols (Neodol 25, available from Shell). Also suitable are unsaturated alcohols such as allyl alcohol; and hydroxy functional esters such as hydroxyethyl acetate and hydroxyethyl acrylate. Preferred are the higher molecular weight monohydroxy compounds, especially nonyl phenol and mixtures of C₁₂ to C₁₅, linear, primary alcohols.

When polyethers a-ii) are present as the sole monofunctional component, they are present in a minimum amount of 0% by weight, preferably 10% by weight, more preferably 20% by weight and most preferably 30% by weight, and a maximum amount of 80% by weight, preferably 70% by weight and more preferably 60% by weight. The preceding percentages are based on the total weight polyethers a).

Suitable isocyanates b-i) include the known monomeric organic diisocyanates represented by the formula, $R(NCO)_2$, in which R represents an organic group obtained by removing the isocyanate groups from an organic diisocyanate having a molecular weight of 112 to 1,000, preferably 140 to 400. Preferred diisocyanates are those represented by the above formula in which R represents a divalent aliphatic hydrocarbon group having from 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having from 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon group having from 7 to 15 carbon atoms or a divalent aromatic hydrocarbon group having 6 to 15 carbon atoms.

Examples of suitable organic diisocyanates include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanato-cyclohexyl)-methane, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanatocyclo-hexyl)-methane, 2,4'-diisocyanato-dicyclohexyl methane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-hexahydro-toluylene diisocyanate, 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, 2,4- and/or 4,4'-diphenylmethane diisocyanate and 1,5-diisocyanato naphthalene and mixtures thereof.

Monomeric polyisocyanates containing 3 or more isocyanate groups such as 4-isocyanatomethyl-1,8-octamethylene diisocyanate and aromatic polyisocyanates such as 4,4',4''-triphenylmethane triisocyanate and polyphenyl polymethylene polyisocyanates obtained by phosgenating aniline/formaldehyde condensates may also be used in an amount of up to 20% by weight, based on the weight of isocyanates b). Also suitable, although less preferred, are polyisocyanate adducts prepared from the

preceding monomeric polyisocyanates and containing isocyanurate, uretdione, biuret, urethane, allophanate, iminooxadiazine dione, carbodiimide and/or oxadiazinetriene groups.

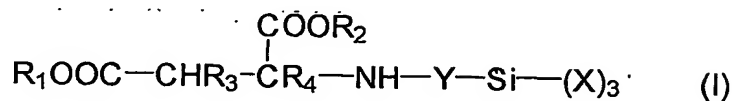
Preferred diisocyanates include bis-(4-isocyanatocyclohexyl)-methane, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, and 2,4- and/or 4,4'-diphenylmethane diisocyanate. Especially preferred are isophorone diisocyanate, 2,4-toluylene diisocyanate and mixtures of 2,4- and 2,6-toluylene diisocyanate.

Diisocyanates b-i) are present in a amount of up to 100% by weight. When monoisocyanates b-ii) are used as the sole monofunctional component, diisocyanates b-i) are present in a minimum amount of 20% by weight, preferably 30% by weight and more preferably 40% by weight, and a maximum amount of 100% by weight, preferably 90% by weight, more preferably 80% by weight and most preferably 70% by weight. The preceding percentages are based on the total weight of isocyanates b).

Suitable isocyanates b-ii) include those corresponding to the formula $R(NCO)$, wherein R is defined as previously set forth with regard to the organic diisocyanates. Suitable monoisocyanates include those corresponding to the diisocyanates previously set forth. Examples include butyl isocyanate, hexyl isocyanate, octyl isocyanate, 2-ethylhexyl isocyanate, stearyl isocyanate, cyclohexyl isocyanate, phenyl isocyanate and benzyl isocyanate.

When monoisocyanates b-ii) are present as the sole monofunctional component, they are present in a minimum amount of 0% by weight, preferably 10% by weight, more preferably 20% by weight and most preferably 30% by weight, and a maximum amount of 80% by weight, preferably 70% by weight and more preferably 60% by weight. The preceding percentages are based on the total weight isocyanates b).

Suitable compounds c) containing reactive silane groups are those corresponding to formula I



wherein

- 5 X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least two of these groups are alkoxy or acyloxy groups, preferably alkyl or alkoxy groups having 1 to 4 carbon atoms and more preferably alkoxy groups,
- 10 Y represents a linear or branched alkylene group containing 1 to 8 carbon atoms, preferably a linear group containing 2 to 4 carbon atoms or a branched group containing 5 to 6 carbon atoms, more preferably a linear group containing 3 carbon atoms,
- 15 R₁ and R₂ are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less, preferably alkyl groups having 1 to 9 carbon atoms, more preferably alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl or butyl groups and
- 20 R₃ and R₄ are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less, preferably hydrogen.
- Especially preferred are compounds in which X represents methoxy, ethoxy groups or propoxy groups, more preferably methoxy or ethoxy groups, and Y is a linear group containing 3 carbon atoms.
- 25 The compounds of formula I are prepared by reacting aminosilanes corresponding to formula V



with maleic or fumaric acid esters corresponding to formula VI



5 Examples of suitable aminoalkyl alkoxysilanes and aminoalkyl acyloxysilanes corresponding to formula V include 3-aminopropyl-triacyloxysilane, 3-aminopropyl-methyldimethoxysilane; 6-aminoethyl-tributoxysilane; 3-aminopropyl-trimethoxysilane; 3-aminopropyl-triethoxysilane; 3-aminopropyl-methyldiethoxysilane; 5-aminopentyl-trimethoxysilane; 5-aminopentyl-triethoxysilane; 4-amino-3,3-dimethyl-butyl-trimethoxysilane; and 3-aminopropyl-triisopropoxysilane. 3-amino-propyl-trimethoxysilane and 3-aminopropyl-triethoxysilane are particularly preferred.

15 Examples of optionally substituted maleic or fumaric acid esters suitable for preparing the aspartate silanes include the dimethyl, diethyl, dibutyl (e.g., di-n-butyl), diamyl, di-2-ethylhexyl esters and mixed esters based on mixture of these and/or other alkyl groups of maleic acid and fumaric acid; and the corresponding maleic and fumaric acid esters substituted by methyl in the 2- and/or 3-position. The dimethyl, diethyl and 20 dibutyl esters of maleic acid are preferred, while the diethyl esters are especially preferred.

 The reaction of primary amines with maleic or fumaric acid esters to form the aspartate silanes of formula III is known and described, e.g., in U.S. Patent 5,364,955, which is herein incorporated by reference.

25 The compounds corresponding to formula I are preferably used as component c). To obtain the benefits of the present invention, they should be present in an amount of at least 10% by weight, preferably at least 30% by weight, more preferably at least 50% by weight and most preferably at least 80% by weight. In addition to the compounds of formula I, which are 30 required according to the present invention, component c) may also

contain aminosilanes that do not correspond to formula I, such as those corresponding to the formula

5 wherein

X and Y are as previously defined and

R₅ represents hydrogen or an organic group which is inert to
isocyanate groups at a temperature of 100°C or less, provided that
R₅ is not a succinate group, preferably hydrogen or an alkyl,
10 cycloalkyl or aromatic group having 1 to 12 carbon atoms and more
preferably an alkyl, cycloalkyl or aromatic group having 1 to 8
carbon atoms, or R₅ represents a group corresponding to formula
VIII

15

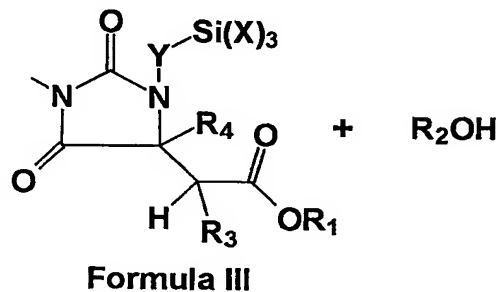
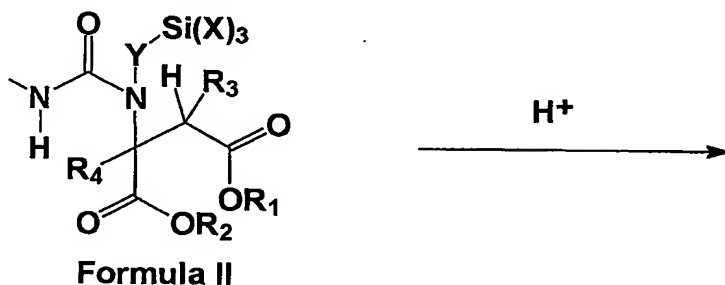


Examples of suitable aminoalkyl alkoxysilanes and aminoalkyl
acyloxysilanes of formula VII, which contain primary amino groups, are the
20 compounds of formula V that have previously been described as suitable
for preparing the aspartate silanes of formula I.

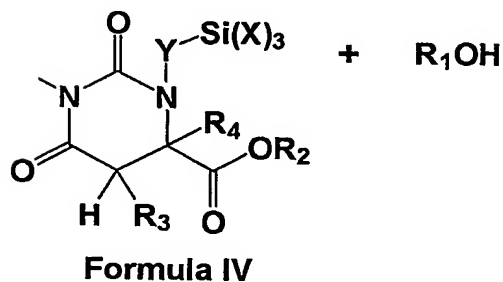
Examples of suitable aminoalkyl alkoxysilanes and aminoalkyl
acyloxysilanes of formula VII, which contain secondary amino groups,
include N-phenylaminopropyl-trimethoxysilane (available as A-9669 from
25 OSI Corporation), bis-(γ-trimethoxysilylpropyl)amine (available as A-1170
from OSI Corporation), N-cyclohexylaminopropyl-triethoxysilane,
N-methylaminopropyl-trimethoxysilane, N-butylaminopropyl-trimethoxy-
silane, N-butylaminopropyl-triacyloxysilane, 3-(N-ethyl)amino-2-methyl-
propyl-trimethoxysilane, 4-(N-ethyl)amino-3,3-dimethylbutyl-trimethoxy-

silane and the corresponding alkyl diethoxy, alkyl dimethoxy and alkyl diacyloxysilanes, such as 3-(N-ethyl)amino-2-methylpropyl-methyl-dimethoxysilane.

The conversion of the non-cyclic urea groups into cyclic urea groups takes place according the following reaction



or



The reaction is carried out in the presence of a catalyst and heat. Suitable catalysts are Brønsted acids, such as mineral acids, carboxylic acids, sulfonic acids and phenols. Preferred catalysts are carboxylic acids, such

as formic acid, acetic acid, propionic acid, 2-ethyl hexanoic acid, malonic acid, phthalic acid, and 1,2,3-tricarboxylic propane. Especially preferred are acetic acid and 2-ethyl hexanoic acid.

Higher temperatures accelerate the conversion of the non-cyclic urea groups into cyclic urea groups. Suitable reaction temperatures are from 50 to 200°C. Very low temperatures require long reaction times and result in a very yellow product. Very high temperatures require only short reaction times, but also result in yellow products. The preferred range for minimizing the development of the yellow color is from 70 to 130°C, more preferably from 90 to 120°C and most preferably from 100 to 120°C.

The conversion of non-cyclic urea groups into cyclic urea groups is accompanied by the release of a mole of alcohol from the succinyl ester. The generated alcohol and the catalyst can be removed from the reaction mixture, for example, by vacuum distillation, or they can be left in the product. If left in the product the released alcohols may undergo a transesterification reaction with the alkoxy groups on the silane. Whether the released alcohols are removed or not is of no consequence, since the products formed with or without vacuum purification, when formulated into a sealant or adhesive, undergo moisture cure to give cured compositions of equivalent performance.

The transesterification reaction can be used to alter the reactivity of the polyether urethanes according to the invention. For example, if a methoxysilane group is converted to an ethoxysilane group or a butoxysilane group, the reactivity of the resulting alkoxysilane groups will be substantially reduced. To the contrary if an ethoxysilane group or a butoxysilane group is converted to a methoxysilane group, the reactivity of the resulting alkoxysilane groups will be substantially increased.

The compositions obtained by the process of the present invention may be cured in the presence of water or moisture to prepare coatings, adhesives or sealants. The compositions cure by "silane polycondensation"

from the hydrolysis of alkoxysilane groups to form Si-OH groups and their subsequent reaction with either Si-OH or Si-OR groups to form siloxane groups (Si-O-Si).

5 Suitable acidic or basis catalysts may be used to promote the curing reaction. Examples include acids such as para-toluene sulfonic acid; metallic salts such as dibutyl tin dilaurate; tertiary amines such as triethylamine or triethylene diamine; and mixtures of these catalysts. The previously disclosed, low molecular weight, basic aminoalkyl trialkoxysilanes, also accelerate hardening of the compounds according to
10 the invention.

 The one-component compositions generally may be either solvent-free or contain up to 70%, preferably up to 60% organic solvents, based on the weight of the one-component composition, depending upon the particular application. Suitable organic solvents include those which are
15 known from either from polyurethane chemistry or from coatings chemistry.

 The compositions may also contain known additives, such as leveling agents, wetting agents, flow control agents, antiskinning agents, antifoaming agents, fillers (such as chalk, lime, flour, precipitated and/or
20 pyrogenic silica, aluminum silicates and high-boiling waxes), viscosity regulators, plasticizers, pigments, dyes, UV absorbers and stabilizers against thermal and oxidative degradation.

 The one-component compositions may be used with any desired substrates, such as wood, plastics, leather, paper, textiles, glass,
25 ceramics, plaster, masonry, metals and concrete. They may be applied by standard methods, such as spraying, spreading, flooding, casting, dipping, rolling and extrusion.

 The one-component compositions may be cured at ambient temperature or at elevated temperatures. Preferably, the moisture-curable
30 compositions are cured at ambient temperatures.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLES

5 Preparation of Silane Functional Aspartate 1

An aspartate resin was prepared according to U.S. Patent 4,364,955. To a 5 liter flask fitted with agitator, thermocouple, nitrogen inlet and addition funnel with condenser were added 1483g (8.27 equivalents) of 3-amino-propyl-trimethoxysilane (Silquest A-1110, available from OSI Corporation). The addition funnel was used to admit 1423.2g (8.27 equivalents) of diethyl maleate over a two hour period. The temperature of the reactor was maintained at 25°C during the addition. The reactor was maintained at 25°C for an additional five hours at which time the product was poured into glass containers and sealed under a blanket of nitrogen. After one week the unsaturation number was 0.6 indicating the reaction was ~99% complete.

Polyether diol 1

A polyoxypropylene diol (Acclaim 12200, unsaturation = 0.007 meq/g available from Bayer Corporation) having a functionality of 2 and an equivalent weight of 5783.

Polyether monool 2

203 g (1.00 eq) of Neodol 25 monool (available from Shell Chemical) were charged to a stainless-steel reactor. Zinc hexacyanocobaltate-tert-butyl alcohol complex (0.143 g, prepared as described in U.S. Patent No. 5,482,908) was added and the mixture was heated with stirring under vacuum at 130°C for one hour to remove traces of water from the monool starter. Propylene oxide (8547 g, 194.2 eq) was introduced into the reactor over 6 hours. After the epoxide addition was completed, the mixture was heated to 130°C until no further pressure

decrease occurred. The product was vacuum stripped and then drained from the reactor. The resulting polyether had an OH number of 6.4, an equivalent weight of 8750, a functionality of 1, and an unsaturation of less than 0.01 meq/g.

5

Example 1 - Preparation of Cyclic Urea/Reactive Silane Terminated Polyurethane (STP) 1 in situ from a 74:26 diol:monool mixture

A 5 liter round bottom flask was fitted with agitator, nitrogen inlet, condenser, heater and addition funnel. Into the flask were charged 127.9 g (1.15 eq) of isophorone diisocyanate, 2691.6g (0.47 eq) of polyether diol 1, 946.7 g (0.11 eq) of polyether monool 2 and 0.78 g of dibutyltin dilaurate. The reaction was heated to 60°C for 8 hours until the NCO content was 0.58% (theoretical = 0.63%). 202.2g (0.55 eq) of silane functional aspartate 1 were added and the flask was heated at 60°C for an additional 1 hour until no NCO remained as determined by an IR spectrum. 19.9 g of glacial acetic acid were added and the temperature was raised to 110°C. The reaction mixture was held at 110°C for three hours until an IR spectrum showed the urea peak had disappeared and a cyclic urea peak had appeared. 19.8 g of vinyl trimethoxysilane were added as moisture scavenger; and 9.9 g of butylated hydroxy toluene and 6.1 g of Naugard 445 (available from Crompton) were added as antioxidants.. The resulting product had a viscosity of 54,000 mPa.s at 25°C.

Comparative Example 2 - Preparation of Non-Cyclic Urea/Reactive Silane Terminated Polyurethane (STP) 2 in situ from a 74:26 diol:monool mixture

A 3 liter round bottom flask was fitted with agitator, nitrogen inlet, condenser, heater and addition funnel. Into the flask were charged 80.0 g (0.72 eq) of isophorone diisocyanate, 1680.4 g (0.31 eq) of polyether diol 1, 591.7 g (0.07 eq) of polyether monool 2 and 0.53 g of dibutyltin dilaurate. The reaction was heated to 60°C for 8 hours until the NCO content was 0.60% (theoretical = 0.62%). 126.4 g (0.34 eq) of silane

functional aspartate 1 were added and the flask was heated at 60°C for an additional 1 hour until no NCO remained as determined by an IR spectrum. 5.5 g of vinyl trimethoxysilane were added as moisture scavenger; and 6.2 g of butylated hydroxy toluene and 3.7 g of Naugard 445 (available from Crompton) were added as antioxidants. The resulting product had a viscosity of 34,700 mPa.s at 25°C.

Heat Aging of Silanes

Into unlined steel cans were placed 300 g of silane. Four cans of each resin were placed into a 90°C oven. One can of each resin was removed each week and the viscosities were determined. The following table sets forth the change in viscosity over the testing period.

Resin	Viscosity profile, cps @ 90°C				
	Initial	1 week	2 weeks	3 weeks	4 weeks
STP 1	421	454	505	449	551
STP 2 (Comparison)	541	448	210	—	194

Formulation of Silane Sealants

The STP's prepared in situ were formulated into sealants using the following typical formulation and procedure.

Procedure

The following is the standard sealant formulation and procedure used to formulate all of the STP's for testing. Values given for each formula component are percent by weight of the total formula weight. A high-speed centrifugal mixer was used to mix the formulation components in the steps given below. Each mixing period was one minute in length at a speed of 2200 rpm.

adhesion promoter. A vinyltrimethoxysilane (Silquest A-171, available from OSI Corporation) was used as the desiccant. The filler used was Specialty Minerals Ultra P Flex precipitated calcium carbonate (mean particle size of 0.07 microns). The catalyst used was dibutyltin dilaurate.

5

Cure and Testing of Silane Sealants

The sealant formulations were cast onto 0.25 inch thick polyethylene sheets and cured at standard conditions of 20°C, 50% relative humidity for at least two weeks before testing. Tensile strength, percent elongation and 100% modulus were determined according to ASTM D-412. Die "C" tear strengths were determined according to ASTM D-624. The results are set forth in the following table.

Examples 3-12: Tensile Properties for sealants prepared from STP 1 and Comparative STP 2

Example		Percent Elongation (%)	Tensile Strength (psi)	100% Modulus (psi)	Tear Strength (pli)
Cyclic Urea STP 1					
3	Initial (No Heat)	244	309	179	31
4	1 Wk @ 70C	259	356	187	31
5	1 Wk @ 90C	256	319	178	32
6	4 Wks @ 70C	265	342	177	34
7	4 Wks @ 90C	288	312	171	32
Urea STP 2					
8	Initial (No Heat)	379	311	144	28
9	1 Wk @ 70C	221	78	46	7
10	1 Wk @ 90C	10	10	10	5
11	4 Wks @ 70C	98	44	39	11
12	4 Wks @ 90C	10	10	10	5

The sealant properties of the preceding examples demonstrate that the polyether urethanes containing terminal cyclic urea/reactive silane groups and prepared by the in situ process according to the invention are more heat stable than the comparative polyether urethanes containing

5 terminal non-cyclic urea/reactive silane groups and prepared by the in situ process.

Although the invention had been described in detail in the foregoing for the purpose of illustration, it was to be understood that such detail was solely for that purpose and that variations can be made therein by those

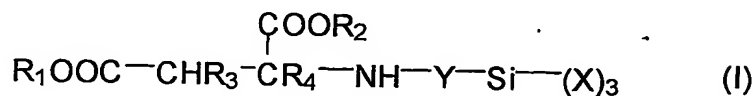
10 skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A process for preparing a moisture-curable, polyether urethane containing terminal cyclic urea/reactive silane groups which comprises reacting at an NCO:OH equivalent ratio of 1.5:1 to 2.5:1
 - 5 a) a hydroxyl component containing
 - 10 i) 20 to 100% by weight, based on the weight of component a), of a polyether containing two hydroxyl groups and one or more polyether segments, wherein the polyether segments have a number average molecular weight of at least 3000 and a degree of unsaturation of less than 0.04 milliequivalents/g, provided that the sum of the number average molecular weights of all of the polyether segments per molecule averages 6000 to 20,000, and
 - 15 ii) 0 to 80% by weight, based on the weight of component a), of a polyether containing one hydroxyl group and one or more polyether segments having a number average molecular weight of 1000 to 15,000, with
 - b) an isocyanate component containing
 - 20 i) 20 to 100% by weight, based on the weight of component b), of a compound containing two isocyanate groups, and
 - 25 ii) 0 to 80% by weight, based on the weight of component b), of a compound containing one isocyanate group,
- provided that total percentages of a-ii) and b-ii) add up to at least 10, to form an isocyanate-containing reaction product and subsequently reacting this reaction product at an equivalent ratio of isocyanate groups to isocyanate-reactive groups of 0.8:1 to 1.1:1 with

- c) a compound containing an isocyanate-reactive group and one reactive silane groups in which at least 10 mole % of component c) is a compound corresponding to the formula

5



10

wherein

X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least two of these groups are alkoxy or acyloxy groups,

15

Y represents a linear or branched alkylene group containing 1 to 8 carbon atoms,

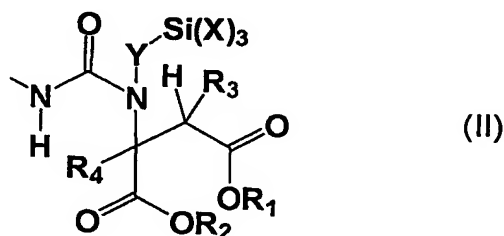
R₁ and R₂ are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less and

20

R₃ and R₄ are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less,

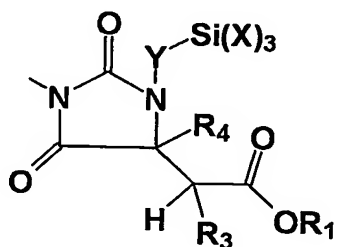
to form an intermediate polyether urethane containing at least a portion of terminal non-cyclic urea/reactive silane groups corresponding to formula II

25

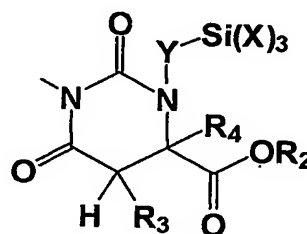


and converting the non-cyclic urea groups to cyclic urea groups by reacting the intermediate polyether urethane in the presence of an acid

catalyst and heat to form terminal cyclic urea/reactive silane groups corresponding to formula III and/or formula IV



Formula III



Formula IV

- 5 2. The process of Claim 1 wherein at least 50 mole % of component c) is a compound corresponding to formula I.
3. The process of Claim 1 wherein at least 80 mole % of component c) is a compound corresponding to formula I and
 - X represents identical or different alkoxy groups having 1 to 4 carbon
 - 10 atoms,
 - Y represents a linear radical containing 2 to 4 carbon atoms or a branched radical containing 5 to 6 carbon atoms and
 - R₁ and R₂ are identical or different and represent alkyl groups having 1 to 4 carbon atoms and
 - 15 R₃ and R₄ represent hydrogen.
4. The process of Claim 1 wherein component a-i) is present in an amount of 20 to 90% by weight, based on the weight of component a); and component a-ii) is present in an amount of 10 to 80% by weight, based on the weight of component a).
- 20 5. The process of Claim 2 wherein component a-i) is present in an amount of 20 to 90% by weight, based on the weight of component a); and component a-ii) is present in an amount of 10 to 80% by weight, based on the weight of component a).
6. The process of Claim 3 wherein component a-i) is present in an amount of 20 to 90% by weight, based on the weight of component a); and component a-ii) is present in an amount of 10 to 80% by weight, based on the weight of component a).
- 25

7. The process of Claim 1 wherein component b-i) is present in an amount of 20 to 90% by weight, based on the weight of component b); and component b-ii) is present in an amount of 10 to 80% by weight, based on the weight of component b).

5 8. The process of Claim 2 wherein component b-i) is present in an amount of 20 to 90% by weight, based on the weight of component b); and component b-ii) is present in an amount of 10 to 80% by weight, based on the weight of component b).

10 9. The process of Claim 3 wherein component b-i) is present in an amount of 20 to 90% by weight, based on the weight of component b); and component b-ii) is present in an amount of 10 to 80% by weight, based on the weight of component b).

15 10. The process of Claim 1 wherein component a-i) is present in an amount of 30 to 80% by weight, based on the weight of component a); component a-ii) is present in an amount of 20 to 70% by weight, based on the weight of component a).

20 11. The process of Claim 2 wherein component a-i) is present in an amount of 30 to 80% by weight, based on the weight of component a); component a-ii) is present in an amount of 20 to 70% by weight, based on the weight of component a).

12. The process of Claim 3 wherein component a-i) is present in an amount of 30 to 80% by weight, based on the weight of component a); component a-ii) is present in an amount of 20 to 70% by weight, based on the weight of component a).

25 13. The process of Claim 1 wherein component b-i) is present in an amount of 30 to 80% by weight, based on the weight of component b); component b-ii) is present in an amount of 20 to 70% by weight, based on the weight of component b).

14. The process of Claim 2 wherein component b-i) is present in an amount of 30 to 80% by weight, based on the weight of component b); component b-ii) is present in an amount of 20 to 70% by weight, based on the weight of component b).

5 15. The process of Claim 3 wherein component b-i) is present in an amount of 30 to 80% by weight, based on the weight of component b); component b-ii) is present in an amount of 20 to 70% by weight, based on the weight of component b).

10 16. The process of Claim 1 wherein the polyether segments of component a-i) have a number average molecular weight of at least 6000 and the polyether segments of component a-ii) have a number average molecular weight of 3000 to 12,000.

15 17. The process of Claim 2 wherein the polyether segments of component a-i) have a number average molecular weight of at least 6000 and the polyether segments of component a-ii) have a number average molecular weight of 3000 to 12,000.

20 18. The process of Claim 3 wherein the polyether segments of component a-i) have a number average molecular weight of at least 6000 and the polyether segments of component a-ii) have a number average molecular weight of 3000 to 12,000.

19. The process of Claim 4 wherein the polyether segments of component a-i) have a number average molecular weight of at least 6000 and the polyether segments of component a-ii) have a number average molecular weight of 3000 to 12,000.

25 20. The process of Claim 10 wherein the polyether segments of component a-i) have a number average molecular weight of at least 6000 and the polyether segments of component a-ii) have a number average molecular weight of 3000 to 12,000.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/38510

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/12 C08G18/28 C08G18/48 C09D175/04 C09J175/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 807 649 A (BAYER AG) 19 November 1997 (1997-11-19) page 2, line 16 -page 4, line 4 examples 1,5	1-20
A	WO 00/26271 A (WILMES OSWALD ;BAYER AG (DE); LEMMERZ RALF (DE); SCHMALSTIEG LUTZ) 11 May 2000 (2000-05-11) cited in the application page 2, line 4 -page 6, line 5 example 1	1-20
A	US 6 265 517 B1 (STUART JONATHAN T) 24 July 2001 (2001-07-24) cited in the application column 5, line 5 -column 6, line 43 example 7; tables 2,3	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

28 April 2004

Date of mailing of the international search report

07/05/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Neugebauer, U

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 03/38510

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0807649	A	19-11-1997	DE 19619538 A1	20-11-1997
			AT 238367 T	15-05-2003
			BR 9703158 A	15-09-1998
			CA 2205106 A1	15-11-1997
			CN 1170009 A , B	14-01-1998
			CZ 9701478 A3	17-12-1997
			DE 59709882 D1	28-05-2003
			DK 807649 T3	11-08-2003
			EP 0807649 A1	19-11-1997
			ES 2196211 T3	16-12-2003
			HU 9700897 A2	28-05-1999
			JP 10053637 A	24-02-1998
			PL 319935 A1	24-11-1997
			TW 479060 B	11-03-2002
			US 5756751 A	26-05-1998
WO 0026271	A	11-05-2000	DE 19849817 A1	04-05-2000
			AT 248872 T	15-09-2003
			AU 743227 B2	24-01-2002
			AU 1152300 A	22-05-2000
			CA 2348566 A1	11-05-2000
			CN 1325413 T	05-12-2001
			CZ 20011504 A3	15-08-2001
			DE 59906898 D1	09-10-2003
			DK 1124872 T3	08-12-2003
			WO 0026271 A1	11-05-2000
			EP 1124872 A1	22-08-2001
			JP 2002528612 T	03-09-2002
			NO 20012033 A	25-04-2001
			PL 347426 A1	08-04-2002
			PT 1124872 T	31-12-2003
			SI 1124872 T1	31-12-2003
			US 6545087 B1	08-04-2003
US 6265517	B1	24-07-2001	NONE	